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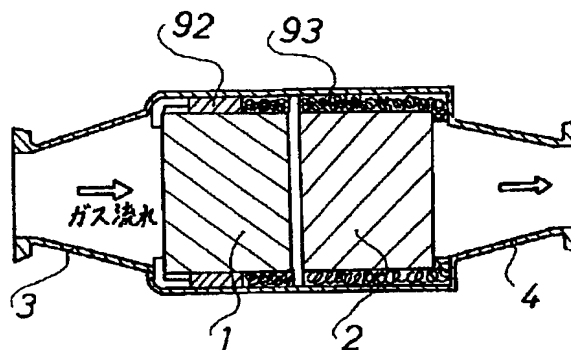
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(54)【発明の名称】 窒素酸化物の除去装置

(57)【要約】

【目的】 低温においても窒素酸化物を効率よく除去する装置を提供する。

【構成】 窒素酸化物を含有するガスの流路の前段にPtまたはPdよりなる触媒層1を設け、後段に $AB'_{1-x}C'_xO_3$ (A:La、Sr、Ce、Ba、Caのうちの少なくとも1種、B':Co、Fe、Ni、Cr、Mn、Mgのうちの少なくとも1種、C':Pt、Pdのうちの少なくとも一方、 $0.005 \leq x \leq 0.2$)で示されるペロブスカイト型構造の物質よりなる触媒層2を設けた装置。



【特許請求の範囲】

【請求項1】 窒素酸化物を含有する気体の流路の前段に設けられた白金またはパラジウムのうちの少なくとも一方を有する第1触媒層と、

該第1触媒層の後段に設けられた $AB'_{1-x}C'_xO$ 、
(Aはランタン、ストロンチウム、セリウム、バリウム、カルシウムのうちの少なくとも1種、B'はコバルト、鉄、ニッケル、クロム、マンガ、マグネシウムのうちの少なくとも1種、C'は白金、パラジウムのうちの少なくとも一方、xは $0.005 \leq x \leq 0.2$ である)で示されるペロブスカイト型構造の物質を有する第2触媒層とよりなることを特徴とする窒素酸化物の除去装置。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、内燃機関や硝酸製造工場等から排出される気体中に含まれる窒素酸化物(NO_x)を除去するための装置に関するものである。

【0002】

【従来の技術】内燃機関や硝酸製造工場等から排出される気体中には窒素酸化物が含まれており、大気汚染の原因となっている。この窒素酸化物を除去する方法として、触媒の還元反応を利用する方法がある。

【0003】従来の触媒を利用した窒素酸化物の除去方法としては、(A)β-アルミナにK、Na、Ca、Ba、La、Ce、Pr等を担持した触媒を利用する方法(特開平4-298235号)、(B)マグネタイト(Fe_2O_3)を還元処理して酸素欠陥を生じさせた活性化マグネタイトよりなる触媒を利用する方法(特開平3-242228号)、あるいは(C)白金アルミナ、銀コバルト酸化物、コバルト酸化物、またはバリウム-鉄複合酸化物等の金属酸化物系の触媒を利用して窒素酸化物を分解する方法(「触媒」31、112(1989))がある。

【0004】しかし、上記の触媒を利用した方法では、以下のような問題点がある。

【0005】まず、(A)の方法では、窒素酸化物を還元するための炭化水素やアルコール類等の還元剤を多量に使用する必要がある(窒素酸化物1モルに対して還元剤0.1~2モル必要である)。

【0006】また、(B)の方法では、活性マグネタイトの酸素欠陥部を使用し終わると該活性マグネタイトが失活するため、持続性に欠ける。

【0007】また、(C)の方法では、窒素酸化物の分解には600℃以上の高温を必要とする。

【0008】さらに、上記のような問題のない方法であり、窒素酸化物の除去方法に類似のものとして、2種類の触媒体を連設した燃焼器がある(特開昭62-218728号)。この燃焼器は、燃焼ガスの流路の前段に白金担持の触媒体を配置し、その後段に白金とアルミナと

希土類金属とがペロブスカイト型構造を形成した触媒体を配置したガスタービン燃焼器である。この燃焼器では、燃料と酸化性気体との混合物からなる燃焼ガスの燃焼温度を上記2種類の触媒により引き下げること(2000℃を900~1200℃にする)により窒素酸化物の発生を減少させるものである。

【0009】

【発明が解決しようとする課題】しかしながら、上記の燃焼器でも以下のような問題点が残っている。

10 【0010】 NO_x の主成分であるNOのN-O間(2.5重結合)の結合エネルギーが極めて大きいため、この結合を切断するのは容易ではない。気相均一系においてNOを分解する活性化エネルギーは 82 kcal/mol と大きいため、気相温度を上げる等の手段によりエネルギーを加えないとNO分解は起きない。後段の触媒体では、この分解活性が低く、しかも吸着能力が小さいため、特に500℃以下のような低温における窒素酸化物の除去効率が低い。これは、後段のペロブスカイト型構造の触媒には、アルミナ含有等により格子欠陥の状態や活性種である白金や希土類元素等の結晶構造における間隔等が適正ではないためである。

【0011】本発明は、上記従来技術の問題点に鑑み込まれたものであり、低温においても窒素酸化物を効率よく除去することができる装置を提供することを目的とする。

【0012】

【課題を解決するための手段】本発明の窒素酸化物の除去装置は、窒素酸化物を含有する気体の流路の前段に設けられた白金またはパラジウムのうちの少なくとも一方を有する第1触媒層と、該第1触媒層の後段に設けられた $AB'_{1-x}C'_xO$ 、(Aはランタン、ストロンチウム、セリウム、バリウム、カルシウムのうちの少なくとも1種、B'はコバルト、鉄、ニッケル、クロム、マンガ、マグネシウムのうちの少なくとも1種、C'は白金、パラジウムのうちの少なくとも一方、xは $0.005 \leq x \leq 0.2$ である)で示されるペロブスカイト型構造の物質を有する第2触媒層とよりなることを特徴とするものである。

【0013】

40 【作用】本発明の装置は、低温においても窒素酸化物を効率よく除去することができる。これは、以下のような作用を呈しているためと推察される。本発明の装置における前段に配置した第1触媒層では、白金またはパラジウムの触媒作用による酸化反応によって、窒素酸化物であるNOが酸化されて NO_2 に変換する。白金またはパラジウムは、その金属表面上の活性点でNOの吸着と活性化、および酸素の吸着と活性化を促進するため上記変換が効率よく行われる。

50 【0014】上記 NO_2 は、後段の第2触媒層で吸着された後、 N_2 、 O_2 、 N_2O 等に分解されて除去され

る。NOガスのN-O結合エネルギーが大きいのでNOの直接分解は起きにくい。前段の第1触媒層でNOより分解しやすいNO_xに変換されるのでNOの除去が促進される。この後段のAB'_{1-x}C'_xO₂で示されるペロブスカイト型構造のC'元素(白金またはパラジウム)は、ペロブスカイト型構造の結晶格子に組み入れられているので、NOからNO_xへの転化活性とNO_xの分解活性が大きく、また、格子欠陥(酸素欠陥部)が生成し、NO_xの吸着量が増大する。

【0015】また、AB'_{1-x}C'_xO₂中のA元素およびB'元素は、本質的にNO_x等の吸着性能に優れたアルカリ土類元素、遷移金属、希土類元素等で構成されているので、白金またはパラジウムの上記作用と相乗的にNO_xの吸着や分解が向上する。

【0016】本発明において上記作用を呈する理由はまだ明らかではないが、該1触媒層のみ、または第2触媒層のみでは効果が不十分であることから、第1触媒層の酸化性能と第2触媒層の分解性能との組み合わせ効果が新たに生じたものであり、この作用は、250~400℃のような低温でも活性が低下しない。特に、低温ではNOの直接分解が起こりにくい。本発明では、一度NOをNO_xに変換した後、吸着や分解によって除去するので有効である。

【0017】

【発明の効果】本発明の装置は、低温においても窒素酸化物を効率よく除去することができる。

【0018】

【実施例】以下、本発明をより具体的に示した具体例を説明する。

【0019】(具体例)本発明の窒素酸化物の除去装置は、図1の例に示すように、窒素酸化物を含む気体の流路の前段に配置された白金またはパラジウムのうちの少なくとも一方よりなる第1触媒層1と、その後段に配置されたペロブスカイト型構造の触媒よりなる第2触媒層2との2種類の触媒層よりなる。図1の例では、窒素酸化物を含む気体を導入するための導入口3と、上記2種類の触媒層により処理した気体を装置外に排出するための排出口4が設けられ、流路の導入口3側に第1触媒層1が配置され、流路の排出口4側に第2触媒層2が配置されている。

【0020】なお、上記第1触媒層と第2触媒層との配置順序を逆にすると、第1触媒層による酸化性能と第2触媒層による分解性能との組み合わせ効果が消失し、低温での活性が生じない。また、第1触媒層または第2触媒層のみ、あるいは第1触媒層の触媒と第2触媒層の触媒との混合体(ベレット形等)では本発明の上記効果は得られない。

【0021】上記前段に配置される第1触媒層の触媒としては、ハニカム形状のコーゼライト等の耐火性無機担体上に白金またはパラジウムのうちの少なくとも一方

を分散担持して触媒としたものが好ましい。

【0022】上記白金またはパラジウムよりなる触媒成分を分散担持する際、該触媒成分をできるだけ高分散化して担持するため、あらかじめアルミナ粉末を耐火無機担体上に担持した後、触媒成分を担持するのが好ましい。このアルミナ粉末は、白金またはパラジウムの吸着点が表面上で均一に分布しているので、白金またはパラジウムの高分散担持の作用を呈する。

【0023】具体的には、アルミナゾル、シリカゾル、ジルコニアゾル等を結合剤として用い、アルミナ粉末をハニカム形状の耐火性無機担体上に被覆し、その後焼成する。結合剤の配合量は、使用状態により異なるが、固形分比で1~10重量%程度がよく、触媒活性を低下させないため必要最低限を選択する。上記焼成後、ジニトロジアンミン白金(またはパラジウム)硝酸溶液等の白金またはパラジウムを含有する溶液を用いて白金またはパラジウムを分散担持する。

【0024】白金またはパラジウムよりなる触媒成分の担持量は、アルミナ粉末に対して0.5~3重量%の範囲が好ましい。3重量%を超えて担持しても触媒成分の粒子が粒子間で凝集を起こし、分散性が悪くなる。また、0.5重量%未満では、触媒成分の活性が生かされにくい。

【0025】なお、第1触媒層の触媒は、上記のようにハニカム形状の他、ベレット形状でもよい。ベレット形状とする場合には、アルミナ粉末に上記と同様の方法により白金またはパラジウムよりなる触媒成分を担持した後、加圧成形し、更に破碎等を行い、ベレット形状とする。

【0026】後段に配置される第2触媒層の触媒としては、AB'_{1-x}C'_xO₂(Aはランタン(La)、ストロンチウム(Sr)、セリウム(Ce)、バリウム(Ba)、カルシウム(Ca)のうちの少なくとも1種、B'はコバルト(Co)、鉄(Fe)、ニッケル(Ni)、クロム(Cr)、マンガン(Mn)、マグネシウム(Mg)のうちの少なくとも1種、C'は白金(Pt)、パラジウム(Pd)のうちの少なくとも一方、xは0.005≤x≤0.2である)で示されるペロブスカイト型構造の物質とする。

【0027】このペロブスカイト型構造の物質は、アルカリ土類金属、遷移金属、希土類元素で構成されており、これら元素は、NO_x吸着性に富むものである。また、異種金属イオンを組み合わせたとき、金属イオンの関係からペロブスカイト型構造はゆがんだ形になり、格子欠陥等が発生してNO_xの吸着性や分解活性が発生する。ペロブスカイト型構造は、熱的に安定であり、耐熱性がある。

【0028】AB'_{1-x}C'_xO₂で示されるペロブスカイト型構造の複合酸化物は、図2に示すような理想格子として単純立方格子の構造(AB'O₆)の結晶格子

B' サイトにC' 元素を組み入れたものである。B' とC' は6個のOに囲まれ、6配位をとる。Aは12個のOに囲まれ、12配位をとる。従って、理想格子とするには、B' とC' は6配位が保てるような原子価を持つと同時にB' とC' のイオン半径ができるだけ近似していることが必要である。B' とC' のイオン半径が異なる程度に応じて結晶格子が歪んだ形になる。更にB' に対してイオン半径の異なるC' の量が増加するにつれて結晶形の歪みが大きくなる。B' とC' のイオン半径の関係によって一義的に決まらないが、上記分子式中のxの値が0.2より大きくなると、歪みが大きくなり、C' が結晶格子中に入らなくなる。一方、xの値が0.005未満でもC' は十分に結晶格子中に入るが、量が少ないため実用上の触媒等の活性種としての効果を発揮しない。

【0029】また、 $AB'_{1-x}C'_xO_3$ 中のC' 元素(Pt, Pd)は、その90%以上が結晶格子中に存在するものがよい。これは、該C' 元素(Pt, Pd)の大部分が粒子として微細化(約2Å)し、触媒等の活性種として分散度が向上し、NO₂の吸着や分解作用が一層効果的となるためである。

【0030】また、 $AB'_{1-x}C'_xO_3$ のペロブスカイト構造において、B'、C' はそれぞれ異なるイオンサイズの格子中にあるため、その組み合わせによってはペロブスカイト構造が適度に歪んでいる。また、B'、C' との原子価が異なる場合、電子補償効果等によって活性が向上する利点がある。これらの場合、ペロブスカイト構造は適度な構造の歪みと格子欠陥を有し、該格子欠陥部等がNO₂の吸着と分解を促進させる。

【0031】このペロブスカイト型構造の物質よりなる触媒は、どのような形状でもよく、例えば、図3および図4に示すような多数のセル24を有するハニカム形状のコーゼライト等の耐火性無機担体22上に該ペロブスカイト型構造の物質21を分散担持したハニカム形状のもの2(更に図4のように、担体22とペロブスカイト型構造の物質21との間にアルミナコート層23を設けてもよい)、あるいはペロブスカイト型構造の物質の粉末をベレット形状に成形したもの等が挙げられる。

【0032】ペロブスカイト型構造の物質をハニカム形状の担体に担持した形態では、該ペロブスカイト型構造の物質の望ましい担持量は、ハニカム形状の担体11容量中に1.0~300g担持するのがよい。この場合、PtまたはPd量がハニカム形状の担体11容量中に0.5~3g担持される。PtまたはPd組成の多いペロブスカイト構造の物質の場合は担持量を少なくするとよい。

【0033】第2触媒層の形成方法としては、ペロブスカイト型構造の物質よりなる触媒を調製し、その後触媒層を形成する方法がある。また、本発明者らが開発した触媒の製造方法もある(特願平4-275019号)。

【0034】この方法について詳細に説明する。

【0035】上記のペロブスカイト型構造の複合酸化物を構成する金属元素の塩とクエン酸とを溶解した水溶液を調製し(第1工程)、該水溶液を乾燥して上記金属元素のクエン酸錯体を形成し(第2工程)、該クエン酸錯体を真空中または不活性ガス中350℃以上で加熱・仮焼成し(第3工程)、その後酸化雰囲気中で焼成する(第4工程)。

【0036】第1工程において、金属元素の塩とクエン酸とを溶解した水溶液を調製する。

【0037】第1工程における金属元素の塩としては、硝酸塩または酢酸塩がよい。これは、第3工程の仮焼成で金属元素以外の残存物を分解できるためである。例えば、塩酸塩の場合、塩素が残存して触媒活性や吸着活性等の特性に影響を与える。

【0038】例えば、ペロブスカイト型構造の複合酸化物($AB'_{1-x}C'_xO_3$)のA元素の硝酸塩としては、La(NO₃)₃・6H₂O、Sr(NO₃)₂・6H₂O、Ba(NO₃)₂・4H₂O等が挙げられ、また、A元素の酢酸塩としては、La(CH₃COO)₃・3/2H₂O、Sr(CH₃COO)₂・1/2H₂O、Ce(CH₃COO)₃・H₂O、Ba(CH₃COO)₂・H₂O等が挙げられる。B' 元素の硝酸塩としては、Co(NO₃)₂・6H₂O、Fe(NO₃)₃・9H₂O等が挙げられる。また、B' 元素の酢酸塩としては、Co(CH₃COO)₂・4H₂O等が挙げられる。C' 元素の硝酸塩としては、ジニトロジアンミン白金硝酸塩、ジニトロジアンミンパラジウム硝酸塩等が挙げられる。また、Pt(NH₃)₄(OH)₂も上記ジニトロジアンミン白金硝酸塩の代用として使用することができる。

【0039】これら金属元素の塩は上記式 $AB'_{1-x}C'_xO_3$ の組成となるような配合割合とする。

【0040】クエン酸の配合量としては、形成するペロブスカイト型構造の複合酸化物1モルに対して2~2.4モルの範囲とするのがよい。該配合量が2モル未満では錯体形成が困難となる場合があり、2.4モルを越えると錯体形成は十分であるが、金属元素の均一混合が困難となる場合がある。

【0041】金属元素の塩とクエン酸とを溶解した水溶液を調製する方法としては、例えば、金属元素の塩をイオン交換水に溶解し、また、別のイオン交換水にクエン酸を溶解し、この両者を混合する方法がある。

【0042】第2工程では、上記水溶液を乾燥することにより金属元素のクエン酸錯体を形成する。

【0043】第2工程における乾燥条件としては、クエン酸錯体が分解しない温度範囲ですみやかに水分を除去する条件(例えば、室温~150℃、2~12時間)が適する。

【0044】第3工程では、上記金属元素のクエン酸錯体を真空中または不活性ガス中350℃以上で加熱して仮焼成する。

【0045】この仮焼成の雰囲気は酸化雰囲気では、クエン酸錯体からのクエン酸および金属元素の塩からの残存物（有機物、硝酸根等）の分解が促進されない。そのため、真空中でも不活性ガス中とする。なお、真空の方が不活性ガスよりも上記分解が促進されるので好ましい。

【0046】加熱温度が350℃未満では、クエン酸および出発原料である金属元素の塩からの残存物（有機物、硝酸根等）が加熱分解できず残存してしまう。また、加熱温度の上限は500℃とするのがよい。500℃を越えても差し支えないが、仮焼成としては500℃までで十分であり、それ以上はエネルギーのムダや仮焼成用装置の損傷が生じるので好ましくない。

【0047】なお、加熱する際、80℃からゆっくり昇温するのがよい。これは、130℃付近からクエン酸および金属元素の塩からの残存物が分解しはじめ、この範囲の温度を時間をかけることにより該分解が促進するためである。350℃以上では約2～3時間ほど保持するのがよい。

【0048】この工程により仮焼成体を形成する。

【0049】第4工程では、上記仮焼成体を焼成する。

【0050】焼成方法としては、どのような方法でもよいが、酸化物を形成するため大気中のような酸素が存在する酸化雰囲気とする。

【0051】また、焼成温度としては、700～950℃の範囲が好ましい。700℃未満の温度においてはペロブスカイト型構造の結晶が成長しにくい。また、950℃を越える温度では、結晶成長が進み過ぎるため、適度な格子欠陥を有して格子内に存在していた貴金属が結晶格子外へ出てしまったり、比表面積が低下して活性が低下するおそれがある。

【0052】また、焼成時間は、1時間程度でも焼成体が得られるが、長時間ほど結晶化率の高い複合酸化物が得られるため、2～5時間が好ましい。

【0053】ペロブスカイト型構造の複合酸化物は、コーゼライト等の耐火性無機担体上に分散担持してハニカム構造の触媒層とするのが好ましい。この分散担持する際、ペロブスカイト型構造の触媒をできるだけ高分散化して担持するため、分散媒体としてPVA（ポリビニールアルコール）やカーボンブラック等を使用するのがよい。また、分散剤や結合剤として、アルミナゾル、シリカゾル、ジルコニアゾル等が使用できる。その使用量としては、目的、使用状態で異なるが、固形分比で3～15重量％程度がよく、触媒活性を低下させないため必要最小限を選択する。

【0054】また、ペロブスカイト型構造の触媒のみからなるペレット状のものを作成する場合には、ペロブス

カイト型構造の触媒の粉末を、加圧成形機等を用いてペレット形状とした後、流通管内に充填して触媒層とする。

【0055】前段の第1触媒層と後段の第2触媒層とは、直接に連結するのが好ましい。また、前段を通過したガス成分が変化しない範囲で後段との間に管を配置してもよい。第1触媒層と第2触媒層との組み合わせたものが複数組連結された場合にはNO_xの除去効果がさらに向上する。

【0056】また、第1触媒層と第2触媒層との触媒の割合について特に限定はない。NO_x中のNO成分の量または全NO_x量に応じて第1触媒層または第2触媒層の触媒量を選択すればよい。

【0057】窒素酸化物を含有する気体を装置内に導入する導入口および処理した気体を排出する排出口は、形状的に特に限定されない。負圧がかからない形状であればよい。

【0058】また、本発明では、図1に示すように、触媒層の周囲にリテーナ91、シール材92、ワイヤーネット93を設けてもよい。

【0059】本発明の装置は、特に酸素過剰下の還元剤の乏しい状態や500℃以下の低温でも高効率で窒素酸化物を除去できるため、ディーゼルエンジンやガソリンエンジン等の内燃機関から排出される排ガス、あるいは硝酸製造工場からの排ガス中の窒素酸化物の除去装置等として利用できる。

【0060】内燃機関から排出される排ガス中の窒素酸化物を除去する場合には、本発明の装置を排気管の途中に配置する。また、パティキュレートフィルターを併用する場合には、本発明の装置の上流側に配置し、また、酸化触媒を併用する場合には、本発明の装置の下流側に配置するとよい。

【0061】以下、本発明の実施例を説明する。

【0062】（実施例）

〔第1触媒の調製〕グレース社製γ-アルミナ粉末100gをビーカーに入れ、イオン交換水300mlを加えてかきまぜた。この溶液に、白金含有量4.47重量％のジニトロジアンミン白金硝酸溶液37.29gとを加え、よくかきまぜた。

【0063】この懸濁液をひきつづきかきまぜながら電気ヒータで加熱し、水分を蒸発させ、白金粒子を均一にアルミナ粉末の表面に分散担持させた。ひきつづき該白金担持アルミナ粉末をろ紙に移し、大気中400℃で1時間加熱して白金担持アルミナ粉末に残留した硝酸根を分解除去することにより灰色の白金担持アルミナ触媒粉末を得た。該触媒粉末の白金含有量はγ-アルミナ粉末120gに対して白金2gであった。

【0064】〔第2触媒の調製〕硝酸ランタン21.67g（0.05モル）をイオン交換水50mlに溶解した。また、酢酸コバルト11.56g（0.045モ

ル)をイオン交換水50mlに溶解した。また、ジニトロジアンミン白金硝酸21.35g(0.005モル)をイオン交換水30mlに溶解した。また、クエン酸25.22g(0.12モル)をイオン交換水120mlに溶解した。これら4種類の水溶液を混合し、約250mlの混合溶液を作製した。

【0065】この混合水溶液をエバポレータで減圧しながら80℃の湯浴中で約4時間かけて蒸発乾固させ、クエン酸錯体を作製した。

【0066】このクエン酸錯体を真空ポンプで減圧(10⁻²torr以下)しながらマントルヒータにより80℃から400℃まで温度が急激に上昇しないようにゆっくり昇温した。なお、130℃付近から酢酸とクエン酸とが分解しはじめた。250~400℃で硝酸根が分解し黄色のガスが発生するので、この発生ガスがなくなることを確認してこの熱処理を完了した(約3時間)。これにより有機物および硝酸根を除去した仮焼成体を作製した。

【0067】この仮焼成体を粉末にした後、ろつばに入れて空気雰囲気中で750℃の温度で3時間焼成した。

【0068】これにより、LaCo_{0.9}, Pt_{0.1}O₃で示される組成のペロブスカイト型構造複合酸化物を製造した。

【0069】また、上記と同様にして、LaFe_{0.9}, Pt_{0.1}O₃、Sr_{0.9}, Ba_{0.1}Co_{0.9}, Pd_{0.1}O₃、La_{0.9}, Sr_{0.1}Cr_{0.9}, Pt_{0.1}O₃、LaNi_{0.9}, Pt_{0.1}O₃で示される組成のペロブスカイト型構造複合酸化物も製造した。

【0070】〔窒素酸化物除去装置の作製〕上記第1触媒、第2触媒いずれの場合も、焼成体の粉末を錠剤成形機で加圧して厚さ約1mmの板状にした後、破碎して粒径1~2mmのペレット状にした。このペレット状の第1触媒10cc(約4g)を内燃機関から排出される排ガスを処理するための流通式固定床の前段に配置し、さらにペレット状の第2触媒10cc(約13g)を流通式固定床の後段に配置した。これにより、図5に示すように、流通式固定床5の先端に設けられ、排ガスを導入するための導入口3と、排ガスの流路の前段部に設けられた第1触媒層1と、その後段部に設けられた第2触媒層2と、流通式固定床5の先端に設けられ、上記2種類の触媒層により処理された排ガスを排出するための排出口4とよりなる窒素酸化物除去装置を作製した。この装置は、導入口3と第1触媒層1との間、および第2触媒層2と排出口4との間に充填触媒が外部に流出しないようにルーバー6が設けられており、導入した排ガスを触媒と接触させ浄化した後、排出するようになっている。流通式固定床5の外周には、ガラスウールよりなる断熱材7が設けられている。また、第1触媒層1、および第2触媒層2には、触媒を充填または取り出すための充填

口8が設けられている。

【0071】〔装置の評価〕上記の装置を用いて、以下のようにNO_xの浄化性能評価試験を行った。

【0072】渦流式ディーゼルエンジン(2.451)の排ガス管に上記装置を、排ガスが導入口3より導入するように配置した。このエンジンを国内10モード試験条件で稼働させて実排ガスを発生させた。空間速度96000/時間で上記実排ガスを装置中に導入し、装置の排出口4におけるNO_x濃度を自動車排ガス分析計

(株)堀場製作所製)で測定した。本装置を使用しない場合のNO_x濃度を基準としてNO_x浄化率を算出した。

【0073】なお、本実施例では、第2触媒の種類を変化させた5種類の形態(実施例1~5)で実施した。

【0074】(比較例1)第1触媒層と第2触媒層との逆設置

第2触媒のペレット10cc(約13g)を流通式固定床5の前段部(排ガス流路の前段)に配置し、第1触媒のペレット10cc(約4g)を流通式固定床5の後段部(排ガス流路の後段)に配置し、その他は上記実施例と同様にした装置を作製し、上記実施例と同様にしてNO_xの浄化性能評価試験を行った。

【0075】(比較例2)第1触媒層の単独設置

第1触媒のペレット20cc(約8g)を流通式固定床5の前段部(排ガス流路の前段)に配置し、流通式固定床5の後段部(排ガス流路の後段)には触媒を配置せず、その他は上記実施例と同様にした装置を作製し、上記実施例と同様にしてNO_xの浄化性能評価試験を行った。

【0076】(比較例3)第2触媒層の単独設置

第2触媒のペレット20cc(約26g)を流通式固定床5の後段部(排ガス流路の後段)に配置し、流通式固定床5の前段部(排ガス流路の前段)には触媒を配置せず、その他は上記実施例と同様にした装置を作製し、上記実施例と同様にしてNO_xの浄化性能評価試験を行った。

【0077】(比較例4)第1触媒と第2触媒との混合体

第1触媒のペレット10cc(約4g)と第2触媒のペレット10cc(約13g)とをよく混合した後、流通式固定床5の前段部(排ガス流路の前段)に配置し、流通式固定床5の後段部(排ガス流路の後段)には触媒を配置せず、その他は上記実施例と同様にした装置を作製し、上記実施例と同様にしてNO_xの浄化性能評価試験を行った。

【0078】上記本実施例および比較例におけるNO_xの浄化性能評価試験の結果を表1に示す。

【0079】

【表1】

| | | 前段触媒 (上流側) | 後段触媒 (下流側) | NO _x 浄化率 (%) |
|-------------|---|---|--|-------------------------------|
| 実 施 例 | 1 | Pt(2g)/ γ -Al ₂ O ₃ (120g) | LaCo _{0.8} Pt _{0.1} O ₃ | 51 |
| | 2 | " | LaFe _{0.8} Pt _{0.2} O ₃ | 59 |
| | 3 | " | LaNi _{0.8} Pt _{0.02} O ₃ | 40 |
| | 4 | " | La _{0.8} Sr _{0.2} Cr _{0.85} Pt _{0.05} O ₃ | 45 |
| | 5 | " | Sr _{0.8} Ba _{0.1} Co _{0.85} Pd _{0.15} O ₃ | 42 |
| 比 較 例 | 1 | LaCo _{0.8} Pt _{0.1} O ₃ | Pt(2g)/ γ -Al ₂ O ₃ (120g) | 16 |
| | 2 | Pt(2g)/ γ -Al ₂ O ₃ (120g) | Pt(2g)/ γ -Al ₂ O ₃ (120g) | 13 |
| | 3 | LaCo _{0.8} Pt _{0.1} O ₃ | LaCo _{0.8} Pt _{0.1} O ₃ | 11 |
| | 4 | ペレット混合 | ペレット混合 | 12 |

【0080】表1より明らかなように、本実施例（実施例1～5）の装置の方が比較例（比較例1～4）のものよりNO_xの浄化性能に優れていることが分かる。

【図面の簡単な説明】

【図1】本発明の窒素酸化物除去装置の一例を示す断面図

【図2】ペロブスカイト構造の結晶格子を示す概念図

【図3】本発明の窒素酸化物除去装置の一例における触媒層を示す斜視図

【図4】本発明の窒素酸化物除去装置の一例における触*

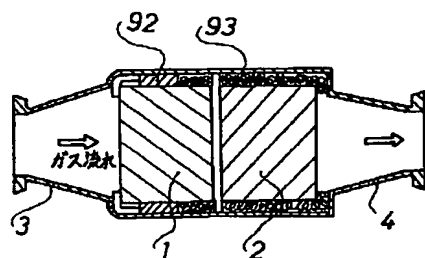
* 媒層を示す断面図

【図5】本発明の実施例における窒素酸化物除去装置を示す断面図

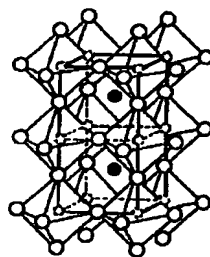
【符号の説明】

- 1 第1触媒層
- 2 第2触媒層
- 3 導入口
- 4 排出口
- 5 流通式固定床

【図1】

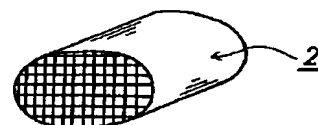


【図2】

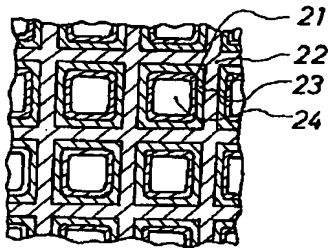


● A元素 ○ B'元素 ○ O

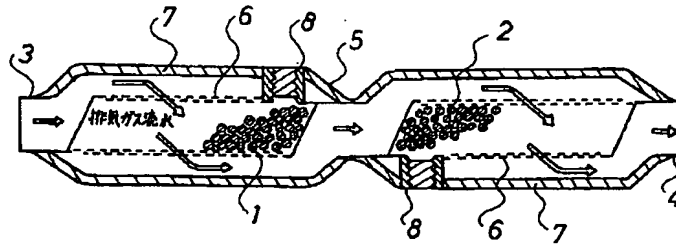
【図3】



【図4】



【図5】



フロントページの続き

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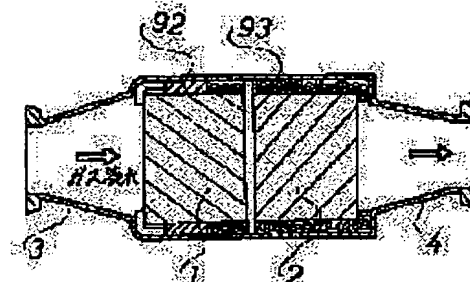
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MIZUNO TATSUJI**(54) APPARATUS FOR REMOVING NITROGEN OXIDE****(57)Abstract:****PURPOSE:** To provide an apparatus for removing efficiently nitrogen oxide at low temp.**CONSTITUTION:** A catalyst layer 1 consisting of Pt or Pd is provided at the front stage of a flow path of a nitrogen oxide-contg. gas and a catalyst layer 2 consists of a substance of perovskite-type structure of $AB'_{1-x}C'O_3$ (wherein A is at least one among La, Sr, Ce, Ba and Ca; B' is at least one among Co, Fe, Ni, Cr, Mn and Mg; C' is at least one of Pt and Pd; (x) is $0.005 \leq x \leq 0.2$) is provided at the rear stage.**LEGAL STATUS**

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CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS
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[Translation done.]

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CLAIMS

[Claim(s)]

[Claim 1] The 1st catalyst bed which has either [at least] the platinum prepared in the preceding paragraph of the passage of the gas containing nitrogen oxides, or the palladium, $AB'_{1-x}C'_xO_3$ (A — a lanthanum —) prepared in the latter part of this 1st catalyst bed At least one sort in strontium, a cerium, barium, and calcium, B' At least one sort in cobalt, iron, nickel, chromium, manganese, and magnesium, C' — the inside of platinum and palladium — at least — on the other hand — $x — 0.005 \leq x \leq 0.2$ — it is — the stripper of the nitrogen oxides characterized by consisting of the 2nd catalyst bed which has the matter of the perovskite type structure shown.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the equipment for removing the nitrogen oxides (NO_x) contained in the gas discharged from an internal combustion engine, a nitric-acid plant, etc.

[0002]

[Description of the Prior Art] Nitrogen oxides are contained in the gas discharged from an internal combustion engine, a nitric-acid plant, etc., and it has become the cause of air pollution. As an approach of removing these nitrogen oxides, there is a method of using the reduction reaction of a catalyst.

[0003] As the removal approach of nitrogen oxides of having used the conventional catalyst (A) How (JP,4-298235,A) to use for beta-alumina the catalyst which supported K, Na, calcium, Ba, La, Ce, Pr, etc., (B) How (JP,3-242228,A) to use the catalyst which consists of activation magnetite which reduction processing of the magnetite (Fe₂O₄) was carried out [magnetite], and produced the oxygen defect, Or there is the approach ("catalyst" 31,112 (1989)) of disassembling nitrogen oxides using the catalyst of metallic-oxide systems, such as (C) platinum alumina, silver cobalt oxide, cobalt oxide, or a barium-iron multiple oxide.

[0004] However, there are the following troubles by the approach using the above-mentioned catalyst.

[0005] First, it is necessary to use reducing agents, such as a hydrocarbon for returning nitrogen oxides, and alcohols, so much by the approach of (A) (it is [0.1-2 mols of reducing agents] required to one mol of nitrogen oxides).

[0006] Moreover, by the approach of (B), since this activity magnetite will deactivate if it finishes using the oxygen defective part of activity magnetite, durability is missing.

[0007] Moreover, by the approach of (C), an elevated temperature 600 degrees C or more is needed for disassembly of nitrogen oxides.

[0008] Furthermore, it is an approach to twist the above problems and the combustor which formed two kinds of catalyst objects successively is in the removal approach of nitrogen oxides as a like (JP,62-218728,A). This combustor is a gas turbine combustor which has arranged the catalyst object of platinum support in the preceding paragraph of the passage of combustion gas, and has arranged the catalyst object with which platinum, the alumina, and the rare earth metal formed perovskite type structure in that latter part. In this combustor, generating of nitrogen oxides is decreased by pulling the combustion temperature of the combustion gas which consists of mixture of a fuel and an oxidizing quality gas according to the two above-mentioned kinds of catalysts, and lowering it (2000 degrees C being made into 900-1200 degrees C).

[0009]

[Problem(s) to be Solved by the Invention] However, also in the above-mentioned combustor, the following troubles remain.

[0010] NO_x Since the binding energy between N-O of NO which is a principal component (2.5-fold association) is very large, it is not easy to cut this association. Unless the activation energy which decomposes NO in a gaseous-phase homogeneous system adds energy with means, such as raising gaseous-phase temperature since it is large, 82 kcal/mol and, NO decomposition does not break out. With a latter catalyst object, this decomposition activity is low, and since the adsorption capacity force is moreover small, the removal effectiveness of the nitrogen oxides in the low temperature following especially 500 degrees C is low. This is because spacing in the crystal structures which are the conditions and active species of a lattice defect by alumina content etc., such as platinum and rare earth elements, etc. is not proper for the catalyst of latter perovskite type structure.

[0011] This invention is made in view of the trouble of the above-mentioned conventional technique, and aims at offering the equipment from which nitrogen oxides are efficiently removable also in low temperature.

[0012]

[Means for Solving the Problem] The 1st catalyst bed which has either [at least] the platinum prepared in the preceding paragraph of the gaseous passage where the stripper of the nitrogen oxides of this invention contains nitrogen oxides, or the palladium, AB_{1-x}C_xO₃ (A — a lanthanum —) prepared in the latter part of this 1st catalyst bed At least one sort in strontium, a cerium, barium, and calcium, B' Cobalt, iron, nickel, chromium, manganese, at least one sort in MAGUNEUSHIMU, C' — the inside of platinum and palladium — at least — on the other hand — x — 0.005<=x<=0.2 — it is — it is characterized by consisting of the 2nd catalyst bed which has the matter of the perovskite type structure shown.

[0013]

[Function] The equipment of this invention can remove nitrogen oxides efficiently also in low temperature. This is guessed because the following operations are presented. In the 1st catalyst bed arranged in the preceding paragraph in the equipment of this invention, NO which is nitrogen oxides oxidizes by the oxidation reaction by the catalysis of platinum or palladium, and it is NO₂. It changes. In order that platinum or palladium may promote adsorption of NO, activation, and adsorption and activation of oxygen in the active spot on the surface of metal, the above-mentioned conversion is performed efficiently.

[0014] Above NO₂ After adsorbing by the 2nd latter catalyst bed, it is decomposed into N₂, O₂, and N₂O etc., and is removed. It is

NO₂ which is easy to decompose from NO by the 1st catalyst bed of the preceding paragraph although direct decomposition of NO cannot break out easily since the N-O binding energy of NO gas is large. Since it is changed, removal of NO is promoted. Since it is included in the crystal lattice of perovskite type structure, AB'C of perovskite type structure shown by 1-x C'x O₃ element (platinum or palladium) of this latter part is NO to NO₂. Inversion activity and NO₂ Decomposition activity is large, and a lattice defect (oxygen defective part) generates, and it is NO₂. The amount of adsorption increases.

[0015] moreover, AB'1-x C'x O₃ — inner A element and B' — an element — essential — NO₂ etc. — since it consists of an alkaline earth element which is excellent in the adsorption engine performance, transition metals, rare earth elements, etc. — the above-mentioned operation of platinum or palladium and multiplication —like — NO₂ Adsorption and decomposition improve.

[0016] Although the reason for presenting the above-mentioned operation in this invention still is not clear, since the effectiveness of this one catalyst bed or just the 2nd catalyst bed is insufficient, the combination effectiveness of the oxidation engine performance of the 1st catalyst bed and the resolvability ability of the 2nd catalyst bed newly arises, and activity does not fall at low temperature [like 250-400 degrees C] whose the operation of this is, either. Although direct decomposition of NO cannot take place especially easily at low temperature, it is NO once at this invention NO₂ After changing, since adsorption and decomposition remove, it is effective.

[0017]

[Effect of the Invention] The equipment of this invention can remove nitrogen oxides efficiently also in low temperature.

[0018]

[Example] Hereafter, the example which made this invention more concrete is explained.

[0019] (Example) The stripper of the nitrogen oxides of this invention consists of two kinds of catalyst beds of the 1st catalyst bed 1 which consists of either [at least] platinum arranged at the preceding paragraph of the passage of the gas containing nitrogen oxides, or the palladium, and the 2nd catalyst bed 2 which consists of a catalyst of the perovskite type structure arranged in the latter part, as shown in the example of drawing 1. In the example of drawing 1, the exhaust port 4 for discharging the gas processed by the inlet 3 for introducing the gas containing nitrogen oxides and the two above-mentioned kinds of catalyst beds out of equipment is formed, the 1st catalyst bed 1 is arranged at the inlet 3 side of passage, and the 2nd catalyst bed 2 is arranged at the exhaust port 4 side of passage.

[0020] In addition, if location sequence of the 1st catalyst bed of the above and the 2nd catalyst bed is made reverse, the combination effectiveness of the oxidation engine performance by the 1st catalyst bed and the resolvability ability by the 2nd catalyst bed will disappear, and the activity in low temperature will not arise. Moreover, the above-mentioned effectiveness of this invention is not acquired in the mixtures (pellet form etc.) of the catalyst of the 1st catalyst bed, the 2nd catalyst bed, or the 1st catalyst bed, and the catalyst of the 2nd catalyst bed.

[0021] What carried out distributed support of either [at least] platinum or the palladium, and was made into the catalyst on fireproof inorganic support, such as cordierite of a honeycomb configuration, as a catalyst of the 1st catalyst bed arranged at the above-mentioned preceding paragraph is desirable.

[0022] In case distributed support of the catalyst component which consists of the above-mentioned platinum or palladium is carried out, in order to decentralize this catalyst component high as much as possible and to support it, after supporting alumina powder on fireproof inorganic support beforehand, it is desirable to support a catalyst component. Since the adsorption site of platinum or palladium is distributed over homogeneity on a front face, this alumina powder presents an operation of high distribution support of platinum or palladium.

[0023] Using alumina sol, a silica sol, a zirconia sol, etc. as a binder, alumina powder is covered on the fireproof inorganic support of a honeycomb configuration, and, specifically, is calcinated after that. Although they change with busy conditions, the loadings of a binder have about 1 - 10 good % of the weight at a solid content ratio, and in order not to reduce catalytic activity, they choose necessary minimum. Distributed support of platinum or the palladium is carried out after the above-mentioned baking using the solution containing platinum or palladium, such as a dinitrodiammine platinum (or palladium) nitric-acid solution.

[0024] The amount of support of the catalyst component which consists of platinum or palladium has 0.5 - 3% of the weight of the desirable range to alumina powder. Even if it supports exceeding 3 % of the weight, a lifting and dispersibility worsen [the particle of a catalyst component] condensation between particles. Moreover, at less than 0.5 % of the weight, the activity of a catalyst component is hard to be employed efficiently.

[0025] In addition, a pellet configuration besides a honeycomb configuration is sufficient as the catalyst of the 1st catalyst bed as mentioned above. In considering as a pellet configuration, after supporting the catalyst component which becomes alumina powder from platinum or palladium by the same approach as the above, pressing is carried out, and crushing etc. is performed further and it considers as a pellet configuration.

[0026] As a catalyst of the 2nd catalyst bed arranged in the latter part AB'1-x C'x O₃ (A — a lanthanum (La) and strontium (Sr) —) At least one sort in a cerium (Ce), barium (Ba), and calcium (calcium), B' Cobalt (Co), iron (Fe), nickel (nickel), chromium (Cr), at least one sort in manganese (Mn) and magnesium (Mg), and C' — the inside of platinum (Pt) and palladium (Pd) — at least — on the other hand — x — 0.005<x<0.2 — it is — it considers as the matter of the perovskite type structure shown.

[0027] The matter of this perovskite type structure consists of alkaline earth metal, transition metals, and rare earth elements, and these elements are NO_x. It is rich in adsorbent. Moreover, when dissimilar metal ion is combined, it becomes the form where perovskite type structure was distorted from the relation of a metal ion, and a lattice defect etc. occurs, and it is NO_x. Adsorbent and decomposition activity occur. Perovskite type structure is thermally stable and has thermal resistance.

[0028] AB'1-x C'x O₃ The multiple oxide of the perovskite type structure shown is an including [in the crystal-lattice B' site of the structure (AB'O₃) of a simple cubic lattice]-as ideal grid as shown in drawing 2 -C' element thing. B' and C' are surrounded by six O and take 6 coordination. A is surrounded by 12 O and takes 12 coordination. Therefore, in order to consider as an ideal grid, while B' and C' have the valence which can maintain 6 coordination, they require that the ionic radius of B' and C' should approximate as much as possible. It becomes the form where the crystal lattice was distorted according to extent from which the ionic radius of B' and C' differs. Distortion of crystal form becomes large as the amount of C' from which an ionic radius furthermore differs to B' increases.

When the value of x in the above-mentioned molecular formula becomes larger than 0.2, distortion becomes large and C' stops entering into a crystal lattice, although not uniquely decided by relation of the ionic radius of B' and C' . On the other hand, less than 0.005, although the value of x fully enters into a crystal lattice, since there are few amounts, as for C' , it does not demonstrate the effectiveness as active species, such as a practical catalyst.

[0029] Moreover, $AB'_{1-x}C'_xO_3$ Inner C' element (Pt, Pd) has that good to which the 90% or more exists in a crystal lattice. This the greater part of C' element (Pt, Pd) makes it detailed as a particle (about 2A), degree of dispersion improves as active species, such as a catalyst, and this is NO2. It is because adsorption and disintegration become much more effective.

[0030] Moreover, $AB'_{1-x}C'_xO_3$ In the perovskite structure, since it is in the grid of the B' and ion size with which C' differs, respectively, depending on the combination, the perovskite structure has been distorted moderately. Moreover, B' and when valences with C' differ, there is an advantage whose activity improves according to an electronic compensation effect etc. In these cases, a perovskite structure has distortion and the lattice defect of moderate structure, and this lattice defect section etc. is NO2. Adsorption and decomposition are promoted.

[0031] The catalyst which consists of matter of this perovskite type structure The thing 2 (still like drawing 4) of the honeycomb configuration which carried out distributed support of the matter 21 of this perovskite type structure on the fireproof inorganic support 22, such as cordierite of a honeycomb configuration which has many cels 24 as what kind of configuration is sufficient as, for example, shown in drawing 3 and drawing 4 Or it may form the alumina coat layer 23 between support 22 and the matter 21 of perovskite type structure, what fabricated the powder of the matter of perovskite type structure in the pellet configuration is mentioned.

[0032] It is good to support the 10–300g of the desirable amounts of support of the matter of this PEROBUZU kite mold structure with the gestalt which supported the matter of perovskite type structure to the support of a honeycomb configuration in 1l. capacity of support of a honeycomb configuration. In this case, Pt or the 0.5–3g of the amounts of Pd are supported in 1l. capacity of support of a honeycomb configuration. In the case of the matter of PEROBUZU kite structure with many Pt(s) or Pd presentations, it is good to lessen the amount of support.

[0033] There is the approach of preparing the catalyst which consists of matter of perovskite type structure as the formation approach of the 2nd catalyst bed, and forming a catalyst bed after that. Moreover, there is also the manufacture approach of the catalyst which this invention persons developed (Japanese Patent Application No. No. 275019 [four to]).

[0034] This approach is explained to a detail.

[0035] The water solution which dissolved the salt and citric acid of the metallic element which constitutes the multiple oxide of the above-mentioned perovskite type structure is prepared (the 1st process), this water solution is dried, the citric-acid complex of the above-mentioned metallic element is formed (the 2nd process), and this citric-acid complex is heated and temporary calcinated above 350 degrees C among a vacuum or inert gas (the 3rd process), and is calcinated by the oxidizing atmosphere after that (the 4th process).

[0036] In the 1st process, the water solution which dissolved the salt and citric acid of a metallic element is prepared.

[0037] As a salt of the metallic element in the 1st process, a nitrate or acetate is good. This is because survival other than a metallic element can be decomposed by temporary baking of the 3rd process. For example, in the case of a hydrochloride, chlorine remains and properties, such as catalytic activity and adsorption activity, are affected.

[0038] for example, as a nitrate of A element of the multiple oxide ($AB'_{1-x}C'_xO_3$) of perovskite type structure $La(NO_3)_3$ and $6H_2O$, $Sr(NO_3)_2$, $Ce(NO_3)_3$ and $6H_2O$, calcium(NO_3)₃, $4H_2O$, etc. are mentioned. As acetate of A element calcium(CH_3COO)₂, $Sr(CH_3COO)_3$ and $[La(CH_3COO)_3 \text{ and } 3/2H_2O, \text{ and }] 1/2H_2O$, $Ce(CH_3COO)_3$ and H_2O , $Ba(CH_3COO)_2$, and H_2O , etc. are mentioned. As a nitrate of B' element, $Co(NO_3)_2$ and $6H_2O$, $Fe(NO_3)_3$, $9H_2O$, etc. are mentioned. Moreover, as acetate of B' element, $Co(CH_3COO)_2$, $4H_2O$, etc. are mentioned. As a nitrate of C' element, a dinitrodiammine platinum nitrate, a dinitrodiammine palladium nitrate, etc. are mentioned. Moreover, $Pt_4(NH_3)_2$ It can be used as substitution of the above-mentioned dinitrodiammine platinum nitrate.

[0039] The salt of these metallic elements is above-mentioned formula $AB'_{1-x}C'_xO_3$. It considers as the blending ratio of coal which is composed.

[0040] It is good to consider as the range of 2–2.4 mols as loadings of a citric acid to one mol of multiple oxides of the perovskite type structure to form. Although complexing is enough if these loadings may become difficult [complexing] in less than two mols and 2.4 mols are exceeded, homogeneity mixing of a metallic element may become difficult.

[0041] As an approach of preparing the water solution which dissolved the salt and citric acid of a metallic element, the salt of a metallic element is dissolved in ion exchange water, and a citric acid is dissolved in another ion exchange water, for example, and there is the approach of mixing these both.

[0042] At the 2nd process, the citric-acid complex of a metallic element is formed by drying the above-mentioned water solution.

[0043] The conditions (for example, room temperature –150 degree C, 2 – 12 hours) which remove moisture as desiccation conditions in the 2nd process in the temperature requirement which a citric-acid complex does not decompose you to be Sumiya are suitable.

[0044] At the 3rd process, temporary baking of the citric-acid complex of the above-mentioned metallic element is heated and carried out above 350 degrees C among a vacuum or inert gas.

[0045] By the oxidizing atmosphere, decomposition of the survival (the organic substance, nitric-acid root, etc.) from the citric acid from a citric-acid complex and the salt of a metallic element is not promoted for the ambient atmosphere of this temporary baking. Therefore, it considers as the inside of inert gas also in a vacuum. In addition, since the above-mentioned decomposition is promoted rather than inert gas, vacuous one is desirable.

[0046] Survival (the organic substance, nitric-acid root, etc.) from the salt of the metallic element whose heating temperature is a citric acid and a start raw material at less than 350 degrees C will not be able to be decomposed thermally, but it will remain. Moreover, the upper limit of heating temperature is good to consider as 500 degrees C. Even if it exceeds 500 degrees C, it does not interfere, but as temporary baking, even 500 degrees C is enough, and since the futility of energy and damage on the equipment for temporary baking arise, more than it is not desirable.

[0047] In addition, in case it heats, it is good to carry out a temperature up slowly from 80 degrees C. This is for the survival from

[from near 130 degree C] a citric acid and the salt of a metallic element to begin to decompose, and for this decomposition to promote the temperature of this range by spending many hours. It is good to hold above 350 degrees C for about about 2 to 3 hours.

[0048] A temporary baking object is formed according to this process.

[0049] the 4th process — the above-mentioned temporary quenching — an adult is calcinated.

[0050] As the baking approach, although what kind of approach may be used, in order to form an oxide, it considers as the oxidizing atmosphere in which oxygen like [in atmospheric air] exists.

[0051] Moreover, as a burning temperature, the range of 700–950 degrees C is desirable. In the temperature of less than 700 degrees C, the crystal of perovskite type structure cannot grow easily. Moreover, at the temperature exceeding 950 degrees C, in order that crystal growth may progress too much, the noble metals which have a moderate lattice defect and existed in the grid come out of a crystal lattice, or there is a possibility that specific surface area may fall and activity may fall.

[0052] Moreover, although a baking object is acquired for at least about 1 hour, since the high multiple oxide of the rate of crystallization is obtained, 2 – 5 hours is as desirable [firing time] as long duration.

[0053] As for the multiple oxide of perovskite type structure, it is desirable to carry out distributed support and to consider as the catalyst bed of honeycomb structure on fireproof inorganic support, such as cordierite. In case [this] distributed support is carried out, in order to decentralize the catalyst of perovskite type structure high as much as possible and to support it, it is good to use PVA (poly vinyl alcohol), carbon black, etc. as a distributed medium. Moreover, alumina sol, a silica sol, a zirconia sol, etc. can be used as a dispersant or a binder. As the amount used, although it differs by the purpose and the busy condition, about 3 – 15 % of the weight is good at a solid content ratio, and in order not to reduce catalytic activity, necessary minimum is chosen.

[0054] Moreover, in creating the thing of the pellet type which consists only of a catalyst of perovskite type structure, it is filled up with it in a flow conduit, and let it be a catalyst bed, after making the powder of the catalyst of perovskite type structure into a pellet configuration using a pressing machine etc.

[0055] As for the 1st catalyst bed of the preceding paragraph, and the 2nd latter catalyst bed, connecting directly is desirable.

Moreover, tubing may be arranged between the latter parts in the range in which the gas constituents which passed the preceding paragraph do not change. It is NOx when two or more sets of combined things of the 1st catalyst bed and the 2nd catalyst bed are connected. The removal effectiveness improves further.

[0056] Moreover, there is especially no limitation about the rate of the catalyst of the 1st catalyst bed and the 2nd catalyst bed. NOx The inner amount or all inner NOx of NO component What is necessary is just to choose the amount of catalysts of the 1st catalyst bed or the 2nd catalyst bed according to an amount.

[0057] Especially the exhaust port that discharges the inlet which introduces the gas containing nitrogen oxides in equipment, and the processed gas is not limited geometrically. What is necessary is just the configuration which does not require negative pressure.

[0058] Moreover, in this invention, as shown in drawing 1, a retainer 91, a sealant 92, and the wire network 93 may be formed in the perimeter of a catalyst bed.

[0059] Even the scarce condition of especially the reducing agent under hyperoxia and the low temperature 500 degrees C or less of the equipment of this invention are efficient, and since nitrogen oxides are removable, it can be used as a stripper of the nitrogen oxides in the exhaust gas discharged by internal combustion engines, such as a diesel power plant and a gasoline engine, or the exhaust gas from a nitric-acid plant etc.

[0060] In removing the nitrogen oxides in the exhaust gas discharged by the internal combustion engine, it arranges the equipment of this invention in the middle of an exhaust pipe. Moreover, when arranging to the upstream of the equipment of this invention in using a particulate filter together, and using an oxidation catalyst together, it is good to arrange to the downstream of the equipment of this invention.

[0061] Hereafter, the example of this invention is explained.

[0062] (Example)

[Preparation of the 1st catalyst] 100g of gamma-alumina powder by the grace company was put into the beaker, and 300ml of ion exchange water was added and stirred. 37.29g of dinitrodiammine platinum nitric-acid solutions of 4.47 % of the weight of platinum contents was added to this solution, and it often wrote and became precocious.

[0063] This suspension was pulled, it heated by the electric heater with continuation stirring, moisture was evaporated, and homogeneity was made to carry out distributed support of the platinum particle on the front face of alumina powder. It pulled, continuation this platinum support alumina powder was moved to the crucible, and gray platinum support alumina catalyst powder was obtained by carrying out decomposition removal of the nitric-acid root which heated at 400 degrees C among atmospheric air for 1 hour, and remained to platinum support alumina powder. The platinum content of this catalyst powder was 2g of platinum to 120g of gamma-alumina powder.

[0064] [Preparation of the 2nd catalyst] 21.67g (0.05 mols) of lanthanum nitrates was dissolved in 50ml of ion exchange water. Moreover, 11.56g (0.045 mols) of cobaltous acetate was dissolved in 50ml of ion exchange water. Moreover, 21.35g (0.005 mols) of dinitrodiammine platinum nitric acids was dissolved in 30ml of ion exchange water. Moreover, 25.22g (0.12 mols) of citric acids was dissolved in 120ml of ion exchange water. These four kinds of water solutions were mixed, and about 250ml mixed solution was produced.

[0065] Evaporation to dryness was carried out over about 4 hours in the 80-degree C water bath, decompressing this mixed water solution by the evaporator, and the citric-acid complex was produced.

[0066] Decompressing this citric-acid complex with a vacuum pump, (10 to 2 or less torrs) the temperature up was slowly carried out so that temperature might not rise rapidly from 80 degrees C to 400 degrees C by the heating mantle. In addition, an acetic acid and a citric acid began to decompose from near 130 degree C. Since the nitric-acid root decomposed at 250–400 degrees C and yellow gas occurred, it checked that this generating gas was exhausted and this heat treatment was completed (about 3 hours). The temporary baking object from which this removed the organic substance and a nitric-acid root was produced.

[0067] After using this temporary baking object as powder, it put into the crucible and calcinated at the temperature of 750 degrees C

by the air ambient atmosphere for 3 hours.

[0068] Thereby, it is $\text{LaCo}_{0.9}\text{Pt}_{0.1}\text{O}_3$. The perovskite type structure multiple oxide of the presentation shown was manufactured. [0069] moreover, the above — the same — carrying out — $\text{LaFe}_{0.8}\text{Pt}_{0.2}\text{O}_3$, $\text{Sr}_{0.9}\text{Ba}_{0.1}\text{Co}_{0.85}\text{Pd}_{0.15}\text{O}_3$, $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.95}\text{Pt}_{0.05}\text{O}_3$, and $\text{LaNi}_{0.98}\text{Pt}_{0.02}\text{O}_3$ The perovskite type structure multiple oxide of the presentation shown was also manufactured.

[0070] [production of a nitrogen-oxides stripper] — the above — after it pressurized the powder of a baking object with the tablet making machine in any case and it made it tabular [with a thickness of about 1mm] the 2nd catalyst the 1st catalyst, it crushed and was made the pellet type with a particle size of 1–2mm. It has arranged in the preceding paragraph of the circulation type fixed bed for processing the exhaust gas discharged by the internal combustion engine in the ten cc (about 4g) of the 1st catalyst of this pellet type, and the ten cc (about 13g) of the 2nd catalyst of a pellet type has been further arranged in the latter part of the circulation type fixed bed. As this showed drawing 5 , it was prepared at the tip of the circulation type fixed bed 5, and it was prepared at the 1st catalyst bed 1 prepared in the pre-stage of the inlet 3 for introducing exhaust gas, and the passage of exhaust gas, the 2nd catalyst bed 2 prepared in the post-stage, and the tip of the circulation type fixed bed 5, and the nitrogen-oxides stripper which consists of an exhaust port 4 for discharging the exhaust gas processed by the two above-mentioned kinds of catalyst beds was produced. The louver 6 is formed so that a restoration catalyst may not flow out outside between an inlet 3 and the 1st catalyst bed 1 and between the 2nd catalyst bed 2 and an exhaust port 4, and this equipment is discharged, after contacting the introduced exhaust gas for a catalyst and purifying it. The heat insulator 7 which consists of glass wool is formed in the periphery of the circulation type fixed bed 5. Moreover, the restoration opening 8 for filling up with or taking out a catalyst is formed in the 1st catalyst bed 1 and the 2nd catalyst bed 2.

[0071] [Evaluation of equipment] Above equipment is used and it is NO_x as follows. The purification performance evaluation test was performed.

[0072] It has arranged so that exhaust gas may introduce the above-mentioned equipment into the exhaust gas pipe of a vortex type diesel power plant (2.45l.) from an inlet 3. This engine was worked by the domestic 10 mode test condition, and real exhaust gas was generated. NO_x [in / the above-mentioned real exhaust gas is introduced into equipment by the 96000/time amount of space velocity, and / the exhaust port 4 of equipment] Concentration was measured with the automobile exhaust analyzer (Horiba Make). NO_x when not using this equipment It is NO_x on the basis of concentration. The rate of purification was computed.

[0073] In addition, at this example, it carried out with five kinds of gestalten (examples 1–5) to which the class of the 2nd catalyst was changed.

[0074] Pellet 10cc (about 13g) of the 2nd catalyst of reverse installation of the 1st catalyst bed and the 2nd catalyst bed is arranged in the pre-stage (preceding paragraph of an emission way) of the circulation type fixed bed 5. (Example 1 of a comparison) Others produce the equipment made to be the same as that of the above-mentioned example by arranging pellet 10cc (about 4g) of the 1st catalyst at the post-stage (latter part of an emission way) of the circulation type fixed bed 5, and it is NO_x like the above-mentioned example. The purification performance evaluation test was performed.

[0075] (Example 2 of a comparison) Others produce the equipment made to be the same as that of the above-mentioned example by arranging pellet 20cc (about 8g) of the 1st catalyst of independent installation of the 1st catalyst bed in the pre-stage (preceding paragraph of an emission way) of the circulation type fixed bed 5, and not arranging a catalyst at the post-stage (latter part of an emission way) of the circulation type fixed bed 5, and it is NO_x like the above-mentioned example. The purification performance evaluation test was performed.

[0076] (Example 3 of a comparison) Others produce the equipment made to be the same as that of the above-mentioned example by arranging pellet 20cc (about 26g) of the 2nd catalyst of independent installation of the 2nd catalyst bed at the post-stage (latter part of an emission way) of the circulation type fixed bed 5, and not arranging a catalyst in the pre-stage (preceding paragraph of an emission way) of the circulation type fixed bed 5, and it is NO_x like the above-mentioned example. The purification performance evaluation test was performed.

[0077] (Example 4 of a comparison) the mixture of the 1st catalyst and the 2nd catalyst, after often mixing pellet 10cc (about 4g) of the 1st catalyst, and pellet 10cc (about 13g) of the 2nd catalyst Others produce the equipment made to be the same as that of the above-mentioned example by arranging in the pre-stage (preceding paragraph of an emission way) of the circulation type fixed bed 5, and not arranging a catalyst at the post-stage (latter part of an emission way) of the circulation type fixed bed 5, and it is NO_x like the above-mentioned example. The purification performance evaluation test was performed.

[0078] NO_x in above-mentioned this example and the example of a comparison The result of a purification performance evaluation test is shown in Table 1.

[0079]

[Table 1]

| | | 前段触媒 (上流側) | 後段触媒 (下流側) | NO _x 浄化率 (%) |
|-------------|---|---|--|-------------------------------|
| 実 施 例 | 1 | Pt(2g)/ γ -Al ₂ O ₃ (120g) | LaCo _{0.9} Pt _{0.1} O ₃ | 51 |
| | 2 | " | LaFe _{0.8} Pt _{0.2} O ₃ | 59 |
| | 3 | " | LaNi _{0.98} Pt _{0.02} O ₃ | 40 |
| | 4 | " | La _{0.8} Sr _{0.2} Cr _{0.95} Pt _{0.05} O ₃ | 45 |
| | 5 | " | Sr _{0.9} Ba _{0.1} Co _{0.95} Pd _{0.05} O ₃ | 42 |
| 比 較 例 | 1 | LaCo _{0.9} Pt _{0.1} O ₃ | Pt(2g)/ γ -Al ₂ O ₃ (120g) | 16 |
| | 2 | Pt(2g)/ γ -Al ₂ O ₃ (120g) | Pt(2g)/ γ -Al ₂ O ₃ (120g) | 13 |
| | 3 | LaCo _{0.9} Pt _{0.1} O ₃ | LaCo _{0.9} Pt _{0.1} O ₃ | 11 |
| | 4 | ペレット混合 | ペレット混合 | 12 |

[0080] The direction of the equipment of this example (examples 1-5) is NO_x from the thing of the example of a comparison (examples 1-4 of a comparison) so that more clearly than Table 1. It turns out that it excels in the purification engine performance.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The sectional view showing an example of the nitrogen-oxides stripper of this invention

[Drawing 2] The conceptual diagram showing the crystal lattice of a perovskite structure

[Drawing 3] The perspective view showing the catalyst bed in an example of the nitrogen-oxides stripper of this invention

[Drawing 4] The sectional view showing the catalyst bed in an example of the nitrogen-oxides stripper of this invention

[Drawing 5] The sectional view showing the nitrogen-oxides stripper in the example of this invention

[Description of Notations]

1 1st Catalyst Bed

2 2nd Catalyst Bed

3 Inlet

4 Exhaust Port

5 Circulation Type Fixed Bed

[Translation done.]

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